SHORT-FORMAT PAPERS

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Acta Cryst. (1989). C**45**, 667–669

Structure of Dicaesium Tetraiodocadmiate(II)

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Abstract. Cs_2CdI_4, $M_r = 885\cdot84$, monoclinic, $P2_1/m$, $a = 7\cdot827\,(1)$, $b = 8\cdot397\,(1)$, $c = 11\cdot050\,(1)$ Å, $\beta = 110\cdot76\,(1)°$, $V = 679\cdot1\,(1)$ Å^3, $Z = 2$, $D_x = 4\cdot332\,(1)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70930 Å, $\mu = 158\cdot0$ cm^{-1}, $F(000) = 740$, $T = 297$ K, $R = 0\cdot029$ for 2734 observed reflections (hemisphere). This work was undertaken in order to explain the motion of the CdI_4^{2-} tetrahedra and the Cs^+ ions in Cs_2CdI_4, which is an Sr_2GeS_4-type structure. The structure contains isolated CdI_4^{2-} tetrahedra with Cd—I bond distances in the range 2·74–2·80 Å. The coordination polyhedra around the Cs^+ ions consist of irregular capped trigonal prisms with 6+2 and 6+3 coordination of I atoms respectively. The Cs—I distances are 3·85–4·28 and 3·77–4·39 Å. The thermal motion of the CdI_4^{2-} tetrahedra and the Cs^+ ions was found to be anharmonic.

Experimental. This work forms part of an investigation of structures of compounds in the CsI—MI_2 system, M = Zn, Cd, Hg. The aim is to study coordination and motion of MI_4^{2-} tetrahedra and Cs^+ ions. Transparent single crystals of Cs_2CdI_4 were grown from a water solution of stoichiometric mixtures of CsI and CdI_2. The crystal used for data collection was as grown and defined by the following planes: {100} (0·056 mm), {001} (0·031 mm), $(0\bar{1}1)$ (0·041 mm), (021) (0·052 mm). Distances in parentheses are from the crystal face to an arbitrarily chosen origin inside the crystal. Cell parameters were obtained by least-squares refinement of 55 reflections with 2θ in the range 26–56°, corrected for absorption effects (Svensson, 1983). Measurements were made on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Intensities of 4447 reflections ($h = -9 \rightarrow 0$, $k = -11 \rightarrow 11$, $l = -14 \rightarrow 15$), $(\sin\theta)/\lambda \leq 0\cdot70$ Å^{-1} were sampled using the ω–2θ scan technique, $\Delta\omega = 0\cdot8° + 0\cdot5°\tan\theta$. Maximum counting time was 240 s. Three standard reflections every 2 h and one orientation reflection every 200 reflections showed no significant variation during data collection (176 h). 2734 reflections with $I > 3\sigma(I)$ were used in refinement, 1472 unique ($R_{\rm int} = 0\cdot045$). No averaging of equivalent reflections was made. Lorentz, polarization and absorption (numerical integration) effects were corrected for. Transmission factors lay between 0·20 and 0·46. Refinement (on F) was started from the parameters found previously for Cs_2HgI_4 (Sjövall & Svensson, 1988). In all calculations isotropic secondary-extinction corrections were included, $g = 1\cdot71\,(5) \times 10^4$, r.m.s. mosaic spread 3·40″ (Becker & Coppens, 1975). Weights were calculated from $w^{-1} = \sigma_c(F_o) + (0\cdot033\,|F_o|)^2 + 2\cdot0$. In the first refinement (I) the harmonic thermal vibration model was assumed. The subsequent difference Fourier map showed residual peaks in the region of every atom. Application of higher-order tensors in the Gram–Charlier expansion of the temperature factors resulted in significantly lower residual electron density. The final refinement (II) included third- and fourth-order coefficients: $\Delta/\sigma \leq 0\cdot090$, average $\Delta/\sigma = 0\cdot009$, $(\Delta\rho)_{\rm max} = 0\cdot9$, $(\Delta\rho)_{\rm min} = -0\cdot7$ e Å^{-3}, $R = 0\cdot029$, $wR = 0\cdot047$, $S = 0\cdot83$, 68 refined parameters. The total number of thermal parameters was reduced by resetting to zero those third- and fourth-order tensor coefficients with magnitude less than $2\cdot5\sigma$. The hypothesis that the atoms vibrate harmonically rather than anharmonically could be rejected at the 99·5% level of confidence on the basis of Hamilton's (1965) $\mathscr{R}$ test: $wR(\mathrm{I})/wR(\mathrm{II}) = 1\cdot202$, $\mathscr{R}_{27,2666,0.005} = 1\cdot010$. Inclusion of fifth-order coefficients in the refinement did not significantly improve wR. The magnitudes of the β-, γ- and δ-tensor coefficients for the I atoms indicate that the entire CdI_4^{2-} tetrahedron is librating. The motion of the Cd atom is almost purely harmonic. For the I atoms the motion is obviously anharmonic with tensor coefficient

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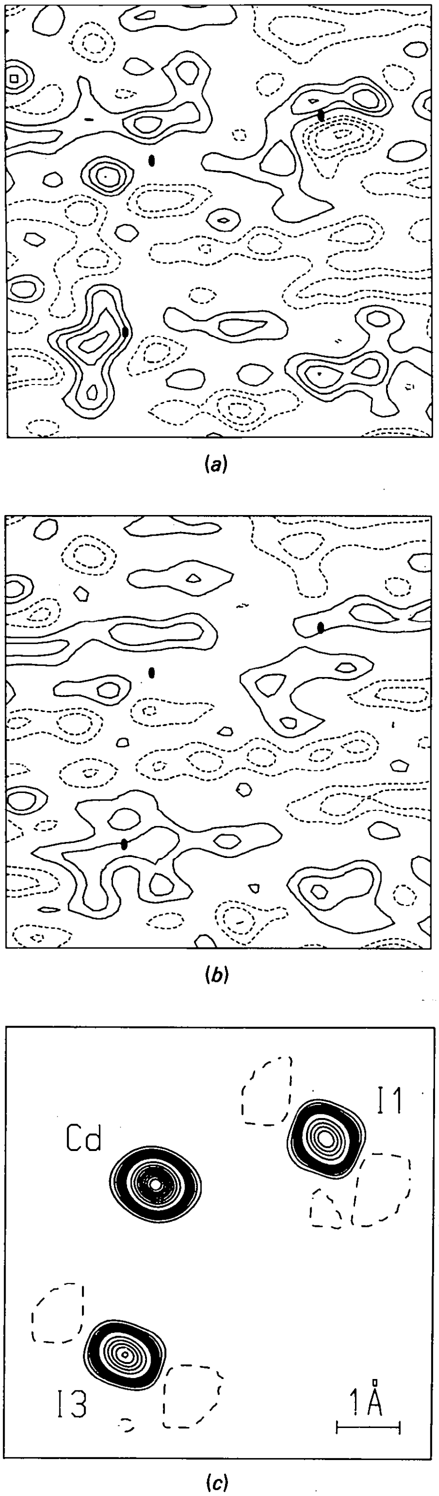

Fig. 1. (*a*) Residual electron density map in the I(3)—Cd—I(1) plane following conventional refinement at 297 K; levels at 0·40 e Å^{-3}. (*b*) The same following refinement including γ- and δ-tensor coefficients. (*c*) Probability density function map given in steps of 1% in the outer part and then from 10% in steps of 10%. For all figures zero contours are omitted and negative contours are dashed.

Table 1. *Final fractional coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Cd	0·08978 (9)	0·25	0·27708 (6)	0·0461 (3)
I(1)	0·18635 (13)	0·25	0·54617 (6)	0·0717 (6)
I(2)	0·25455 (13)	0·51188 (4)	0·21362 (8)	0·0556 (3)
I(3)	−0·27962 (12)	0·25	0·14433 (8)	0·0750 (5)
Cs(1)	0·65900 (15)	0·25	0·46797 (8)	0·0552 (2)
Cs(2)	0·22180 (15)	0·25	0·90736 (13)	0·0677 (4)

Table 2. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cd—I(3)	2·740 (1)	Cs(2)—I(3)	3·852 (1)
Cd—I(2)	2 × 2·763 (1)	Cs(2)—I(1)	3·901 (2)
Cd—I(1)	2·796 (1)	Cs(2)—I(2)	2 × 3·967 (1)
		Cs(2)—I(2)	2 × 4·019 (1)
Cs(1)—I(3)	3·773 (1)	Cs(2)—I(3)	2 × 4·283 (1)
Cs(1)—I(2)	2 × 3·892 (1)		
Cs(1)—I(1)	3·906 (2)		
Cs(1)—I(2)	2 × 4·056 (1)		
Cs(1)—I(1)	4·087 (2)		
Cs(1)—I(1)	2 × 4·388 (1)		
I(3)—Cd—I(2)	2 × 111·30 (3)	I(2)—Cd—I(2)	105·50 (4)
I(3)—Cd—I(1)	113·92 (4)	I(2)—Cd—I(1)	2 × 107·18 (3)

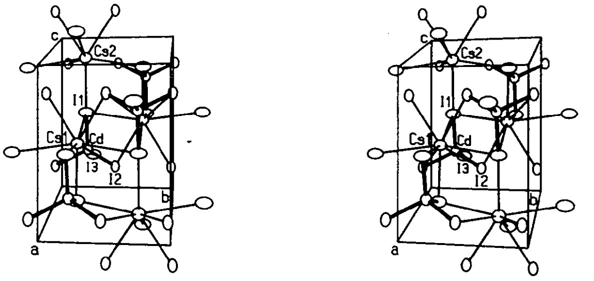

Fig. 2. Stereoview of the structure of Cs_2CdI_2 projected 10° off [100]. The coordination around the Cs ions is shown by adding I atoms of CdI_4^{2-} tetrahedra from neighbouring cells.

magnitudes as large as 18σ for I(1), γ_{122}, and 14σ for I(3), γ_{223}. The maximum values for Cs(1)$^+$ and Cs(2)$^+$ were 4σ, γ_{223}, and 13σ, γ_{122}, respectively. Residual electron density maps and a probability density function map of the atoms in the I(3)—Cd—I(1) plane are shown in Figs. 1(*a*)–(*c*).

Scattering factors and anomalous-dispersion corrections for Cs$^+$, Cd and I were taken from *International Tables for X-ray Crystallography* (1974). The computer programs used were described by Lundgren (1982). Final atomic coordinates and temperature factor coefficients are given in Table 1* and bond

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* Lists of structure factors, anisotropic and anharmonic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51511 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances and angles in Table 2. A stereoview of the unit cell is shown in Fig. 2.

Related literature. A monoclinic structure of Cs_2CdI_4 in polar space group $P2_1$ was assumed by Zandbergen, Verschoor & IJdo (1979). Subsequent measurements of dielectric properties (Gesi, 1985) for the three related compounds Rb_2ZnI_4, Tl_2ZnI_4 and Cs_2HgI_4 with Sr_2GeS_4-type structure indicated a non-polar space group at room temperature. Powder data for α-Cs_2CdI_4, room-temperature phase, were recently reported by Touchard, Louër & Louër (1986). Their results are in good agreement with those of the present work and those of Sjövall & Svensson (1988) on refinement of Cs_2HgI_4. The space group and unit-cell parameters given by Aleksandrov, Mel'nikova & Kokov (1987) do not agree with those in this paper.

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A (2-Amino-2-methylpropanedioato)(Optically Active Cyclen)cobalt(III) Complex*

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Abstract. *cis*-(*SSSR*)-β_1-[(*R*)-2-Amino-2-methylmalonato](2*R*,5*R*,8*R*,11*R*-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane)cobalt(III) perchlorate 2·5-hydrate, $[Co(C_4H_5NO_4)(C_{16}H_{36}N_4)]ClO_4.2{\cdot}5H_2O$, $M_r = 619{\cdot}00$, triclinic, $P1$, $a = 10{\cdot}455\,(5)$, $b = 31{\cdot}715\,(15)$, $c = 10{\cdot}492\,(7)$ Å, $\alpha = 110{\cdot}50\,(5)$, $\beta = 116{\cdot}74\,(5)$, $\gamma = 80{\cdot}36\,(5)°$, $U = 2910\,(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}410$, $D_x = 1{\cdot}415$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}74$ mm^{-1}, $F(000) = 1316$, $T = 296$ K, final $R = 0{\cdot}068$ for 7646 unique reflections with $|F_o| > 3\sigma(|F_o|)$. The geometries of the four independent molecules in the unit cell are essentially the same. In each octahedral molecule, the Co^{III} ion is surrounded by four N of the macrocycle, and by N and O atoms of *pro-R* carboxylate in the amino acid. The uncoordinated carboxyl group forms an intramolecular hydrogen bond to one of the N atoms in the macrocyclic ligand, in molecule 1 [N(1)—H···O(17)2: 2·98 (1) Å, ∠N(1)—H···O(17)2: 159 (12)°].

Experimental. The crystal was obtained from the same reaction product as the monoclinic one whose structure had already been reported (Tsuboyama, Takishima, Sakurai & Tsuboyama, 1987). The density was measured by flotation in CCl_4–benzene. Details of data collection and structure refinement are given in Table 1. Structure solved by direct methods with *MULTAN*78 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Calculations performed using the program system *UNICS*-III (Sakurai & Kobayashi, 1979) on a FACOM M-780. The four independent molecules are labelled 1, 2, 3 and 4. The molecular geometries of these are almost identical to that of the monoclinic crystal. The H atom attached to

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* Part 9 of the series *Metal Complexes of Chiral Cyclen.* Part 8: Tsuboyama, Takishima, Sakurai & Tsuboyama (1987).

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